GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: April 6, 1976

Project Title: ~~Research Initiation~~ -Application of Crown Ethers in Industrial Anionic Polymerizations

Project No: E-27-638

Project Director: Dr. Fred L. Cook

Sponsor: National Science Foundation

Agreement Period: From 4/1/76 Until 3/31/78

Type Agreement: Grant ENG 76-10141

Amount: $20,000 NSF
5,662 GIT E-27-314
$25,662 TOTAL

Reports Required:
Annual Letter Technical, Final Report

Sponsor Contact Person (s):

Technical Matters

Contractual Matters
(thru OCA)

Mr. Gaylord L. Ellis
Grants Officer
National Science Foundation
Washington, D.C. 20550
(202) 632-5965

Defense Priority Rating:

Assigned to: Textile Engineering (School/Laboratory)

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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

Date: 12/4/78

Project Title: ~~Research Initiation~~ - Application of Crown Ethers in Industrial Anionic Polymerizations

Project No: E-27-638

Project Director: Dr. Fred L. Cook

Sponsor: National Science Foundation

Effective Termination Date: 3/31/78

Clearance of Accounting Charges: 3/31/78

Grant/Contract Closeout Actions Remaining:

_ Final Invoice and Closing Documents
X Final ~~Fiscal Report~~ XXXXXXXXX Fiscal Accounting (FCTR)
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_ Govt. Property Inventory & Related Certificate
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Assigned to: Textile Engineering (School/Laboratory)

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CA—4 (3/76)

RESEARCH INITIATION - APPLICATION OF CROWN ETHERS IN INDUSTRIAL ANNIONIC POLYMERIZATIONS

Annual Technical Letter Report

National Science Foundation
Engineering Division
Engineering Chemistry and Energetics Section
Washington, D. C. 20550

April 1, 1976 - March 31, 1977

Prepared Under Grant No. ENG76-10141

by the

Georgia Institute of Technology
Atlanta, Georgia 30332

Dr. Fred L. Cook
Author and Investigator
School of Textile Engineering

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APPLICATION OF CROWN ETHERS IN INDUSTRIAL ANIONIC POLYMERIZATIONS

Non-Technical Annual Summary

Dr. Fred L. Cook

Macrocyclic polyethers (crown ethers) are compounds that have the ability to accelerate certain reactions in organic solvents, and therefore are projected to be useful in industrial systems employing such reactions to polymerize caprolactam, isoprene, and styrene. Polymerizations have been conducted using butyl lithium-crown ether as a catalyst system for isoprene and styrene, and sodium caprolactam-crown ether as a catalyst system for caprolactam. With styrene and isoprene, best results have been obtained by mixing the monomer with crown ether in benzene, followed by injection of the butyl lithium catalyst (1.8:1, butyl lithium to crown ether ratio) and shaking at room temperature. The caprolactam was polymerized by dissolving sodium sand in the bulk monomer, adding crown ether, and plunging the system in a hot bath at 185-260°C.

Styrene polymerized extremely rapidly in the presence of crown ether, giving a 100% conversion in 1 minute with crown present. The molecular weight of the polystyrene was found to increase proportionately with the amount of crown ether present. Isoprene polymerization was much slower under similar conditions, forming a tacky polymer. Heat-transfer problems were encountered in the caprolactam polymerizations, resulting in incomplete conversion before modification. Studies comparing butyl sodium with butyl lithium as initiators and employing various crown ethers are planned.

APPLICATION OF CROWN ETHERS IN INDUSTRIAL ANIONIC POLYMERIZATIONS

Technical Annual Report

Dr. Fred L. Cook

The initial stage of the research involved synthesizing and purifying substantial quantities of the macrocyclic polyethers to be used in the subsequent polymerization studies: 1, 4, 7, 10, 13, 16 - hexaoxacyclooctadecane (18-crown-6); 1, 4, 7, 10, 13 - pentaoxacylopentadecane (15-crown-5); and 1, 4, 7, 10 - tetraoxacyclododecane (12-crown-4). The hole sizes of these crown ethers are optimum for complexation of potassium, sodium, and lithium, respectively. The synthetic approach was that of Cook, Liotta, et al., utilizing a modified Williamson ether synthesis.[1,2] The general synthetic approach had been the same for all three synthesis,[1] i.e., formation of the alkoxide of glycol ethers with a "template" metal base, followed by Sn2 reaction with a dichloride ether. The overall yields reported in the earlier work were low (25% for 18-crown-6, 14% for 15-crown-5, and 13% for 12-crown-4). Substantial effort in the current research was therefore placed on improving the yields of the crown ether syntheses. Variables that were manipulated were:

1. Reaction temperatures
2. Solvents
3. Alkoxide formation times and temperatures

The latter variables was considered to be crucial, as only short times (15-20 minutes) were used in the initial papers to equilibrate the alkoxide system after the metal hydroxide was added to the glycol ether

solutions.[1,2] Earlier reports on syntheses of linear alcohols from lower glycols and dichlorides, in which the proper "template effect" necessary for cyclization was absent,[3] had recommended heating of the alkoxide solution for 6 hours at 100°C, cooling to 72°C, and then adding the dichloride either reagent.[4] Presumably, less free hydroxide was available in the system to displace the primary chlorides and to promote elimination. Numerous reaction sequences were run in which the stated variables were altered, both alone and in various combinations. The yields obtained in the modified runs were not significantly higher than those reported, ranging at best 10% higher. Sufficient quantities of the three crown ethers were isolated, purified and characterized to satisfy the polymerization requirements of the project in these initial studies.

Since the project began, two papers have appeared that offer improved syntheses of unsubstituted crown ethers. Dale and Daasvatn have utilized a boron trifluoride-etherate system with a template salt to control the cyclopolymerization of ethylene oxide to specific crown ethers.[5] Johns and coworkers have used shorter (and cheaper) dichloride ether compounds with longer glycol ethers to form 18-crown-6 and 15-crown-5 in improved yields using the Williamson route.[6] The Dale approach appears especially suited for large-scale production, which improves the potential for commercial adaptation of the polymerization modifications investigated in the current research.

It has also been discovered in recent months that unsubstituted 12-crown-4 is not as effective in complexing lithium as was projected in earlier reports, while benzo-14-crown-4 has been shown to complex lithium

very well.[7,8] The 14-crown-4 has been postulated to have the optimum hole size for the lithium cation.[9] If samples of the benzo-14-crown-4 can be obtained,[8] comparison of the polymerization effects of the new crown ether with 12-crown-4 and 15-crown-5 in lithium-based systems will be assessed. An attempt was made in the current research to synthesize unsubstituted 14-crown-4 using excess ethylene glycol, NaOH, and 1,3-dichloropropane. As of the reporting date no unsubstituted 14-crown-4 has been isolated. Continued work on the detailed synthetic route is planned, with several alternate routes also under consideration.

For the polymerization studies with crown ethers, the monomers and solvents were vigorously purified and dried using conventional techniques.[10] The extremely hygroscopic crown ethers were dried by stirring the crowns with molecular sieves, subjecting the systems to high vacuum for long periods of time, sealing off the samples under vacuum, and storing the compounds in a desicator under nitrogen or vacuum.[11]

The polymerization systems consisted of solvent, catalyst, crown ether, and monomer. The systems investigated thus far are:

1. isoprene-heptane-butyl lithium-15-crown-5
2. isoprene-benzene-butyl lithium-15-crown-5
3. styrene-benzene-butyl lithium-15-crown-5
4. caprolactam-sodium metal-18-crown-6

The reactions were carried out in glass polymerization tubes capped with a rubber septum for injection of the butyl lithium solution. Blanks with no crown ether present were run concurrently with each of the systems to assess the effect of the crown ether. The isoprene-heptane systems, with or without crown ether, did not polymerize to any

great extent. Rigorous drying of the 15-crown-5 and further purification of the heptane mixture used as the solvent did not significantly improve the polymer yield. Apparently, reactive impurities in the heptane mixture were being carried through the purification steps, and the catalyst was being destroyed before polymerization. A switch to purified benzene gave a good yield of polymer for the systems without crown. Further studies are underway with 15-crown-5 in benzene. Pure n-heptane has been obtained to define if inseparable impurities in the original heptane mixture caused premature termination in the isoprene polymerizations.

Styrene polymerization offered the most substantial proof of crown enhancement of polymerization characteristics discovered to date. The components of a typical system were as follows:

Benzene	Styrene	15-Crown-5	n-Buli
15 ml.	0.04 moles	0.414 mmoles	0.73 mmoles

The catalyst was injected at room temperature, and the sealed tube shaken initially for 70 hours. The resulting reaction was highly exothermic, requiring external cooling to keep the system below 70°C. In a series of experiments in which only the concentration of crown was varied, a straight-line relationship was observed between the inherent viscosity (and hence molecular weight) of the polystyrene obtained and the amount of crown in the system. A 100% conversion to polymer was observed in all cases. A rate experiment was performed in which identical polymerizations with and without 15-crown-5 were run for only 5 minutes before quenching with methanol. The results were as follows:

System	η_{inh} (dl/g)	Yield (%)
with 15-C-5	0.188	100
without 15-C-5	0.041	16

The same experiment was repeated with the crown ether present and reaction allowed to proceed only 1 minute before methanol quench-precipitation. Inherent viscosity of 0.179 dl/g was obtained, with 100% yield of polymer.

Caprolactam polymerizations have been hampered by heat transfer problems. Initial studies, utilizing 18-crown-6 and the sodium salt of caprolactam at 260°C as the catalyst system, typically resulted in low polymer yields ($\sim$ 55%) and relatively low viscosities (η_{inh} = 0.84 dl/g) due to incomplete polymerization. Woods metal was employed as a heat transfer medium, and recent results without crown ether have given high polymer yields.

The remainder of the project will be directed towards companion styrene and isoprene systems containing n-BuLi with 15-crown-5 and 12-crown-4 as the crown components. If possible, benzo-14-crown-4 will also be compared. The styrene and isoprene polymerizations will also be initiated by n-BuNa with 15-crown-5 and 18-crown-6, and the sodium-based systems compared with the lithium catalysts. Comparison studies on butadiene will be undertaken when the styrene/isoprene investigations are well defined. An optimum system will be defined for all three alkene monomers. The caprolactam polymerizations will be directed toward lower temperature of reaction and shorter times. Typical caprolactam anionic polymerizations require high temperatures (200°C - 260°C), and the stability of the crown ethers at these temperatures in the presence of the catalyst will be examined.

Bibliography

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4. S. Z. Perry and H. Hibbert, Can. J. Res., 14B(3), 77 (1936).
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11. F. L. Cook, Diss. Abstracts, B, 37(1), 222 (1976).

APPLICATION OF CROWN ETHERS IN INDUSTRIAL ANIONIC POLYMERIZATIONS

Annual Report - Most Significant Accomplishment

Dr. Fred L. Cook

The most significant research recomplished during the reporting period has been the elucidation of the extreme effect that macrocyclic polyether cationic complexing agents (crown ethers) have on the polymerization characteristics of the styrene-benzene-butyl lithium system. Polymer grade styrene (0.04 moles), benzene (15 ml.), and 1, 4, 7, 10, 13 - pentaoxacyclopentadecane (15-crown-5, 0.414 mmoles) were sealed in a pressure polymerization tube under nitrogen with a rubber septum. The butyl lithium-heptane solution (0.73 mmoles BuLi) was injected through the septum into the tube, and the tube shaken at ambient temperature. Methanol was used to terminate the reaction and precipitate the polymer. Blanks were run under identical conditions but without the crown ether included.

Rate and molecular weight studies were conducted utilizing the styrene system. When the butyl lithium catalyst was injected into the polymerization tube at room temperature, a strong exotherm evolved, requiring external cooling in some cases. A orange-red tint developed in systems without crown ether on catalyst introduction, while systems containing 15-crown-5 converted to a yellow tint as the quantity of crown ether was increased. The colors indicated carbanion formation, while the color change with crown concentration reflected an alteration of electron density around the carbanion by virtue of the counterion complexation.

The rate studies consisted of gradually decreasing the time of reaction before methanol quench-precipitation and analyzing the percent conversion. A 5 minute reaction time produced the following results:

System	ηinh (dl/g)	Yield (%)
with 15-C-5	0.188	100
without 15-C-5	0.041	16

A 1 minute reaction time with crown produced similar results (ηinh = 0.174 dl/g, 100% conversion), indicating that the polymerization is apparently near instantaneous. As predicted, the "naked" butyl carbanion is a extremely potent nucleophile in the presence of crown ether. The crown, by virtue of complexation with the lithium cation, is apparently promoting solvent-separated ion pair formation, resulting in a low-solvated carbanion of extreme reactivity. Studies to further define the time of polymerization of styrene in the presence of crown ether are underway.

In the molecular weight studies, a series of experiments were run in which only the quantity of 15-crown-5 was altered. The butyl lithium: crown ratio was gradually raised from no crown to 1.8:1, the polymerizations run under the same conditions, and the resulting polymers analyzed for percent conversion and inherent viscosity. All the systems resulted in a 100% conversion to polymer. A plot of ηinh vs. quantity of 15-crown-5 in grams at a fixed butyl lithium concentration resulted in a linear plot (Figure 1). The complexation of the lithium cation by the crown ether apparently stabilizes the carbonion at the end of the chain, which favors propagation over disproportionation - termination. Studies to narrow the butyl lithium: crown ether molar ratio are planned to find the limiting

value of the linear relationship and to determine the complexation ratio.

The preliminary investigations with styrene polymerizations in the presence of 15-crown-5 have demonstrated the following:

1. The 15-crown-5 hole size is apparently more compatible with the lithium cation than has been previously reported in thoretical studies, as the results of this research indicate good complexation behavior between the two species.

2. The rate of styrene polymerization is extremely rapid in the presence of 15-crown-5, being much faster than with butyl lithium alone, and apparently being almost instantaneous.

3. Up to the butyl lithium: crown ratio investigated to date (1.8:1), a straight line relationship exists between the inherent viscosity of the polystyrene and the quantity of crown ether utilized in the polymerization.

The research results indicate that in-mold polymerization of styrene with the crown-butyl lithium catalyst system may be feasible. The extremely rapid rate of polymerization and ability to "tailor" the molecular weight by the crown concentration offers molding capabilities. Another potential commercial application is in copolymerization of styrene with unsaturated polyester resins, a common system used in molding of fiber glass reinforced composites. Both in-mold polymerization with styrene and application to fiber glass composites offer significant opportunities for crown ethers to make a meaningful technological impact on engineering practice and industry.

INHERENT VISCOSITY OF POLYSTYRENE
AS A FUNCTION OF CROWN CONCENTRATION

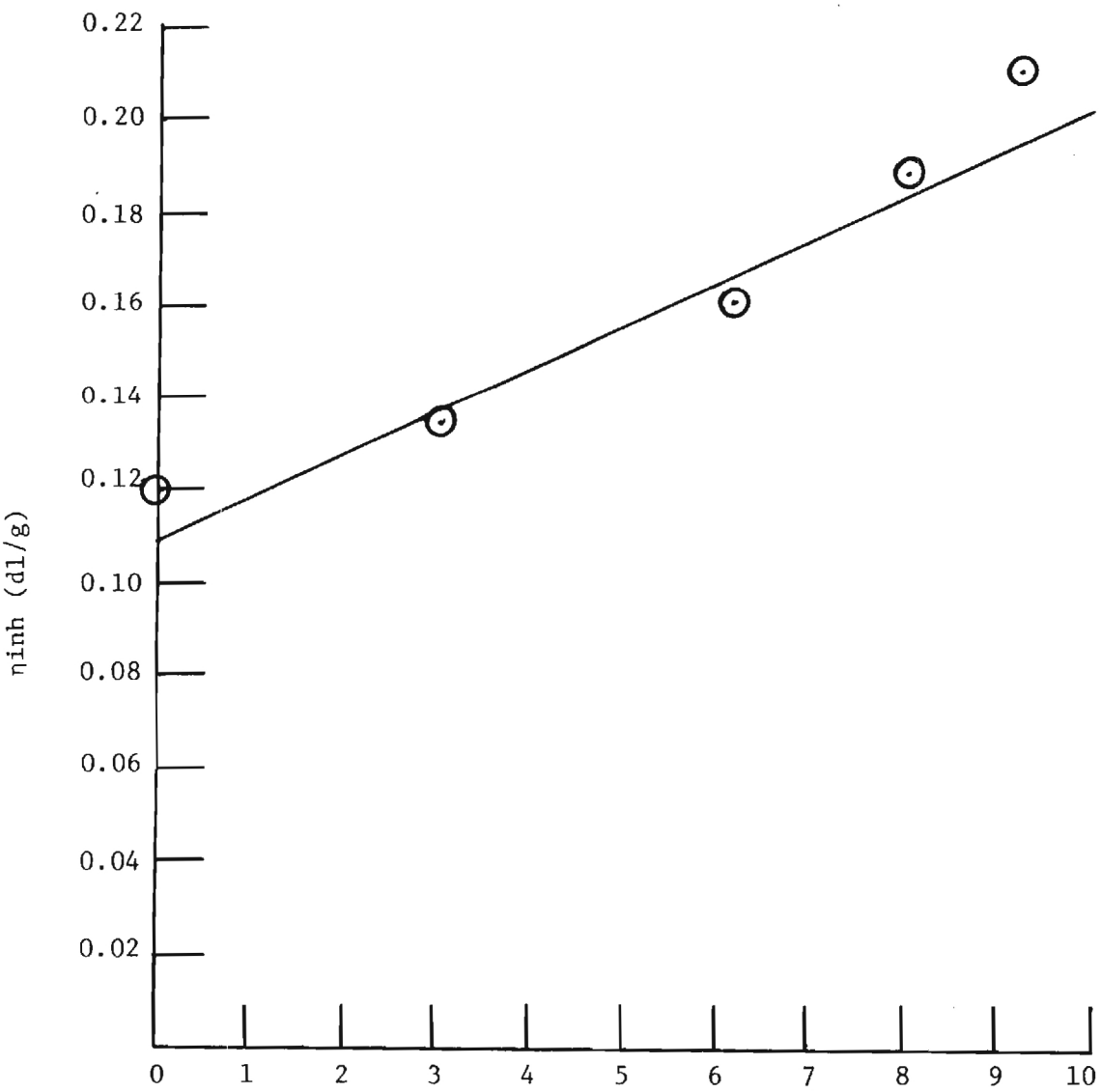

Figure 1

APPLICATION OF CROWN ETHERS IN INDUSTRIAL ANIONIC POLYMERIZATIONS

Annual Report-Auxiliary Personnel

Dr. Fred L. Cook

In addition to the Principal Investigator, two students have participated in the project. Mr. Kenneth Domeshek, an undergraduate, was supported through the project in the summer of 1976. Ken participated in the studies aimed at improving yields, isolating and purifying the crown ethers utilized in the polymerization research. He also aided in the initial attempts to synthesize unsubstituted 14-crown-4, and purified many of the solvents and reagents needed in the polymerization studies. Kenneth thus made substantial contributions to the project while expanding his own research capabilities and expertise.

Mr. Thomas Montgomery has chosen the project as his M.S. thesis topic. Tom has been supported through the School of Textile Engineering, and not through the research. He has been invaluable in the initial polymerization studies, offering numerous suggestions to alter the approaches and proving to be an excellent experimentalist. Tom has gained from the project valuable experience in polymerization techniques and polymer analysis that he was lacking, and as a result has broadened his career opportunities and capabilities as a Chemist.

APPLICATION OF CROWN ETHERS IN INDUSTRIAL ANIONIC POLYMERIZATIONS

Annual Report-Papers, Presentations, Awards

Dr. Fred L. Cook

Dr. Fred L. Cook, Principal Investigator on the project, has expanded his professional activities considerably during the 1976-1977 reporting period. Dr. Cook has obtained two additional sponsored projects:

1. "Energy Conservation in the Textile Industry, Phases I and II", Principal Investigator, ERDA ($356,000).
2. "Preparation and Analyses of Chemically Sorptive Yarns from Rayon and Acrylic Precursors", Principal Investigator, U.S. Army-Natick Laboratories ($20,000).

He has made numerous invited presentations including:

1. F. L. Cook, "Energy Consumption by Wet Process", National Meeting, Textile Information Users Council, Atlanta, GA., October 7, 1976.
2. F. L. Cook, "Breakdown of Energy Required in Dyeing and Finishing", Short Course, College of Textiles, N. C. State University, Raleigh, N. C., September 15, 1976.
3. F. L. Cook, "Energy Consumption by Wet Process", Annual Meeting, Textile Operating Executives, Atlanta, GA., October 23, 1976.
4. F. L. Cook, "How to Conserve Energy in Wet Processing", EES Energy Conservation Systems Workshop for Plant Engineers, Dalton, GA., October 19, 1976.

5. F. L. Cook, "Fundamentals of Textile Finishing", Short Course, American Association of Textile Chemists and Colorists, Southeastern Section, Atlanta, Georgia, December 3, 1976.
6. F. L. Cook, "Energy Consumption by Process in Dyeing and Finishing", Short Course, Clemson University, Clemson, S. C., January, 12, 1977.
7. F. L. Cook and W. C. Tincher, "Dyebath Reuse in Carpet Beck Dyeing", ACS National Meeting, New Orleans, LA., March 21, 1977.
8. F. L. Cook, "Energy Programs at Georgia Tech", Short Course, Clemson University, Clemson, S. C., March 8, 1977.
9. F. L. Cook, "Preparation and Synthetic Utilizations of Crown Ethers", Chemistry Department, Berry College, Rome, GA., April 20, 1977.

Dr. Cook has had the following papers accepted for publication in the 1976-77 reporting year:

1. F. L. Cook and W. C. Tincher, "Dyebath Reuse in Carpet Beck Dyeing", Cellulose, Paper and Textile Chemistry Preprints, ACS, 173, 1 (1977).
2. F. L. Cook, "I. Synthesis and Thermal Characteristics of Polyacrylonitrile Models. II. Reactions of Potassium Cyanide Solubilized in Aprotic Solvents by 18-Crown-6 Macrocylic Polyether, Crystalline Complexes of 18-Crown-6 with Various Nitrile Compounds, and Synthesis of 12-Crown-4", Dissertation Abstracts, B, 37(1), 222 (1976).
3. F. L. Cook, et al., "Macrocyclic Polyether: 18-Crown-6 Polyether", Organic Syntheses, 57, Proc. No. 1934 (1977).

Copies of any papers relevant to the supported project will be forwarded to NSF when available.

Dr. Cook has recently been elected as a Full Member to Sigma Xi, the Scientic Research Society of North America. He is also a member of the Delta Kappa Phi Textile Honorary Fraternity, Tau Beta Pi Engineering Honorary Fraternity, American Chemical Society, and the American Association of Textile Chemists and Colorists.

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APPLICATION OF CROWN ETHERS IN INDUSTRIAL ANIONIC POLYMERIZATIONS

Non-Technical Final Summary

Dr. Fred L. Cook

Particular chemicals called crown ethers have the ability to accelerate various reactions in organic solvents, and therefore were projected to be useful in industrial polymerization systems with styrene, isoprene, butadiene, and caprolactam. Polymerizations have been conducted using butyl lithium-crown ether as a catalyst system for styrene, isoprene, and butadiene, and using sodium caprolactam-crown ether for caprolactam.

Dramatic modifications in the polymerization characteristics of the styrene and isoprene were observed upon the addition of crown ether. With both polymers, the rate of polymerization and also the final molecular weight were increased significantly over conventional systems containing no crown ether. The increases were less dramatic with the isoprene than with the styrene system. The results indicate that in-mold polymerization of liquid styrene monomer by the use of crown ethers may be feasible, avoiding costly and energy-intensive process steps inherent in conventional molding operations with polystyrene.

Butadiene, which is a gas at room temperature, gave only a low-molecular weight polymeric oil on polymerization in the crown ether system. Residual water, oxygen, and other impurities in the condensed butadiene apparently terminated the polymerizations prematurely.

Attempts to modify the bulk polymerization of caprolactam by addition of crown ethers proved unsuccessful due to degradation of the crown ethers under the polymerization conditions. Likewise, substitution of butyl sodium for butyl lithium in the styrene and isoprene polymerizations was unsuccessful due to crown ether degradation.

APPLICATION OF CROWN ETHERS IN INDUSTRIAL ANIONIC POLYMERIZATIONS

Technical Final Report

Dr. Fred L. Cook

The initial stage of the research involved synthesizing and purifying substantial quantities of the macrocyclic polyethers to be used in the subsequent polymerization studies: 1, 4, 7, 10, 13, 16 - hexaoxacyclooctadecane (18-crown-6); 1, 4, 7, 10, 13 - pentaoxacyclopentadecane (15-crown-5); and 1, 4, 7, 10 - tetraoxacyclododecane (12-crown-4). The hole sizes of these crown ethers are optimum for complexation of potassium, sodium, and lithium, respectively. The synthetic approach was that of Cook, Liotta, et al., utilizing a modified Williamson ether synthesis.[1,2] The general synthetic approach had been the same for all three syntheses,[1] i.e., formation of the alkoxide of glycol ethers with a "template" metal base, followed by Sn2 reaction with a dichloride ether. The overall yields reported in the earlier work were low (25% for 18-crown-6, 14% for 15-crown-5, and 13% for 12-crown-4). Substantial effort in the current research was therefore placed on improving the yields of the crown ether syntheses. Variables manipulated were:

1. Reaction temperatures
2. Solvents
3. Alkoxide formation times and temperatures.

The latter variables were considered to be crucial, as only short times (15-20 minutes) were used in the initial papers to equilibrate the alkoxide system after the metal hydroxide was added to the glycol ether solutions.[1,2] Earlier reports on syntheses of linear alcohols from lower glycols and dichlorides, in which the proper "template effect" necessary for cyclization was absent,[3] recommended heating of the alkoxide solution for six hours at 100°C, cooling to 72°C, and then adding the dichloride ether reagent.[4] Presumably, less free hydroxide was available in the system to displace the primary chlorides and to promote elimination. In numerous reaction sequences the stated variables were altered both alone and in various combinations. The yields obtained in the modified runs

were not significantly higher than those reported, ranging approximately 10% higher. Sufficient quantities of the three crown ethers were isolated, purified and characterized to satisfy the polymerization requirements of the project in these initial studies.

For the polymerization studies with crown ethers, the monomers and solvents were vigorously purified and dried using conventional techniques.[5] The extremely hygroscopic crown ethers were dried by stirring the crown ethers with molecular sieves, subjecting the systems to high vacuum for long periods of time, sealing off the samples under vacuum, and storing the compounds in a desicator under nitrogen or vacuum.[6] The n-BuLi (Aldrich) was assessed for concentration every two weeks by the method of Gilman and Cartledge,[7] and n-BuNa was synthesized by the method of Lochmann.[8] Viscosity measurements were by simple U-tube viscometry, and the $\overline{Mv}$ values were calculated from intrinsic viscosities by use of the Mark-Staudinger-Houwink relationship and literature $\underline{K}$ and $\underline{a}$ values.[9]

The polymerization systems consisted of solvent, ether and monomer. The systems investigated were:

1. styrene-benzene-butyl lithium-15-crown-5 and 12-crown-4
2. styrene-benzene-butyl sodium-18-crown-6
3. isoprene-heptane-butyl lithium-15-crown-5 and 12-crown-4
4. isoprene-heptane-butyl sodium-18-crown-6
5. caprolactam-sodium caprolactam-18-crown-6
6. butadiene-heptane-butyl lithium-12-crown-4.

The reactions were carried out in glass polymerization tubes capped with a rubber septum for injection of the butyl lithium solutions. $\underline{n}$-BuNa was added as a solid. Blanks with no crown ether present were run concurrently with each of the systems to assess the effect of the crown ether. The concentrations of both the n-BuLi and the crown ethers were varied, and the effects on the rates of polymerization and molecular weights were determined.

Styrene polymerization gave substantial proof of crown ether enhancement of polymerization characteristics. The following typical example gave complete conversion to polymer in less than ten seconds (least measurable time of reaction) at 25°C:

Benzene	Styrene	15-Crown-5	n-BuLi
15 ml	43 Mmoles	0.189 Mmoles	0.74 Mmoles

In an identical system without crown ether, a period of twenty minutes was required to complete polymerization. The rate was slower on substitution of 12-crown-4 for 15-crown-5 in the same system, but was still much more rapid than with no crown ether (Figure 1). For isoprene, the rate of reaction was also accelerated dramatically, though less than styrene, in comparison to systems without crown ethers (Figure 2).

The molecular weight of both polystyrene and polyisoprene increased on addition of 15-crown-5 and 12-crown-4. With styrene, a peak was reached in $\overline{Mv}$ enhancement as the crown ether concentration was increased, with further addition of crown ether lowering the molecular weight (Figure 3). The peak was reached with both crown ethers at a molar ratio of 0.5:1 (crown:n-BuLi). Apparently, the activation of crown ether-complexed chain ends was so intense that monomer depletion did not allow time to grow long chain lengths when the activated ends were present in greater than 50% proportion, resulting in decreased $\overline{Mv}$ from the peak value. Polyisoprene followed similar curves initially (Figure 4), but molar ratios greater than 0.32:1 (crown: n-BuLi) resulted in formation of a yellow-brown precipitate and no polymer. The precipitate was apparently crown ether or a crown ether complex with either the n-BuLi or short "living" oligomers. Hexane is a solvent for recrystallization of 18-crown-6,[3] confirming the low solubility of crown ethers in non-polar alkane solvents.

The research results indirectly confirmed that 15-crown-5 is a more effective complexing agent for lithium cation than is 12-crown-4. The larger crown ether produced greater increases in molecular weights and rates of polymerization in all systems tested.

The addition of crown ethers to systems containing n-BuNa instead of n-BuLi produced no detectable beneficial effects on styrene and isoprene polymerizations. The n-BuNa was relatively insoluble in heptane, limiting its utility. Also, NMR studies indicated that the initiator attacked the ether linkages of the crown excessively under mild conditions.

Attempts to modify the bulk polymerization of caprolactam at several temperature ranges through the use of crown ethers also proved unsuccessful. The crown ethers were unstable at the temperature required to

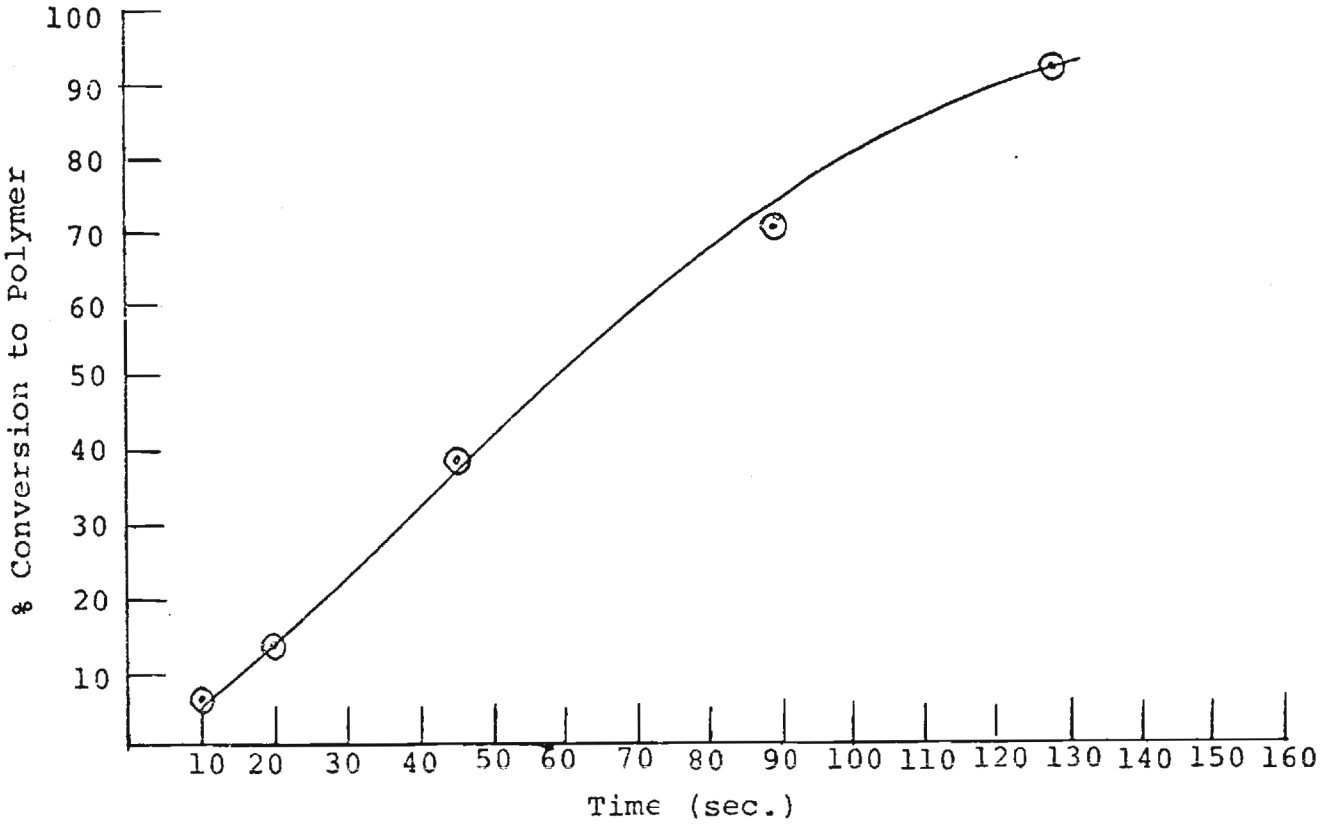

FIGURE 1. Overall Rate Study for Polymerization of Styrene Using 12-Crown-4. Each Reaction contained 0.035g of 12-Crown-4 (.01M).

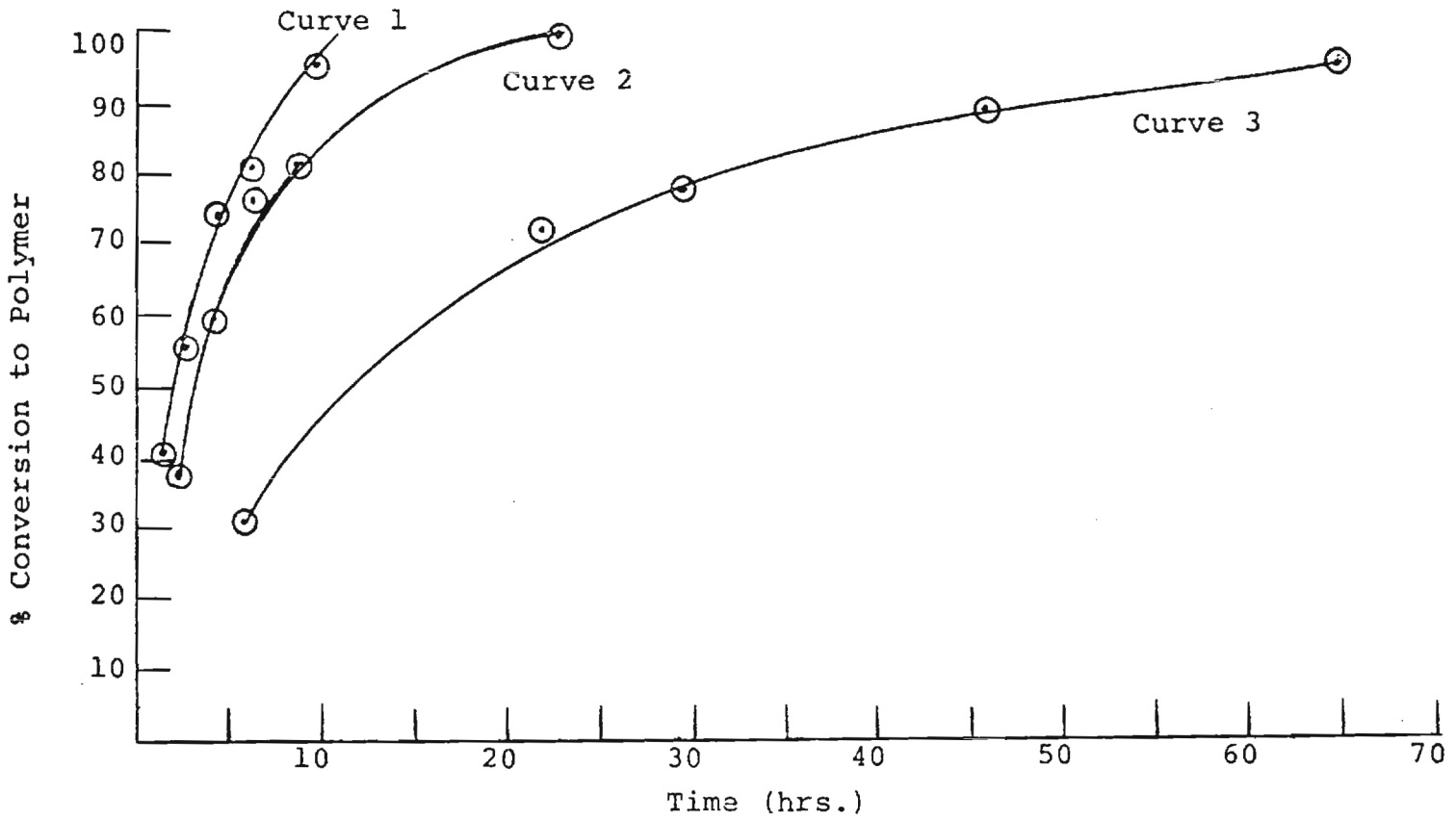

FIGURE 2. Plots of % Conversion to Polymer vs. Time for Isoprene Polymerization Systems Containing 0.114 Mmoles of 15-Crown-5 (Curve 1), 0.114 Mmoles of 12-Crown-4 (Curve 2), and No Crown (Curve 3).

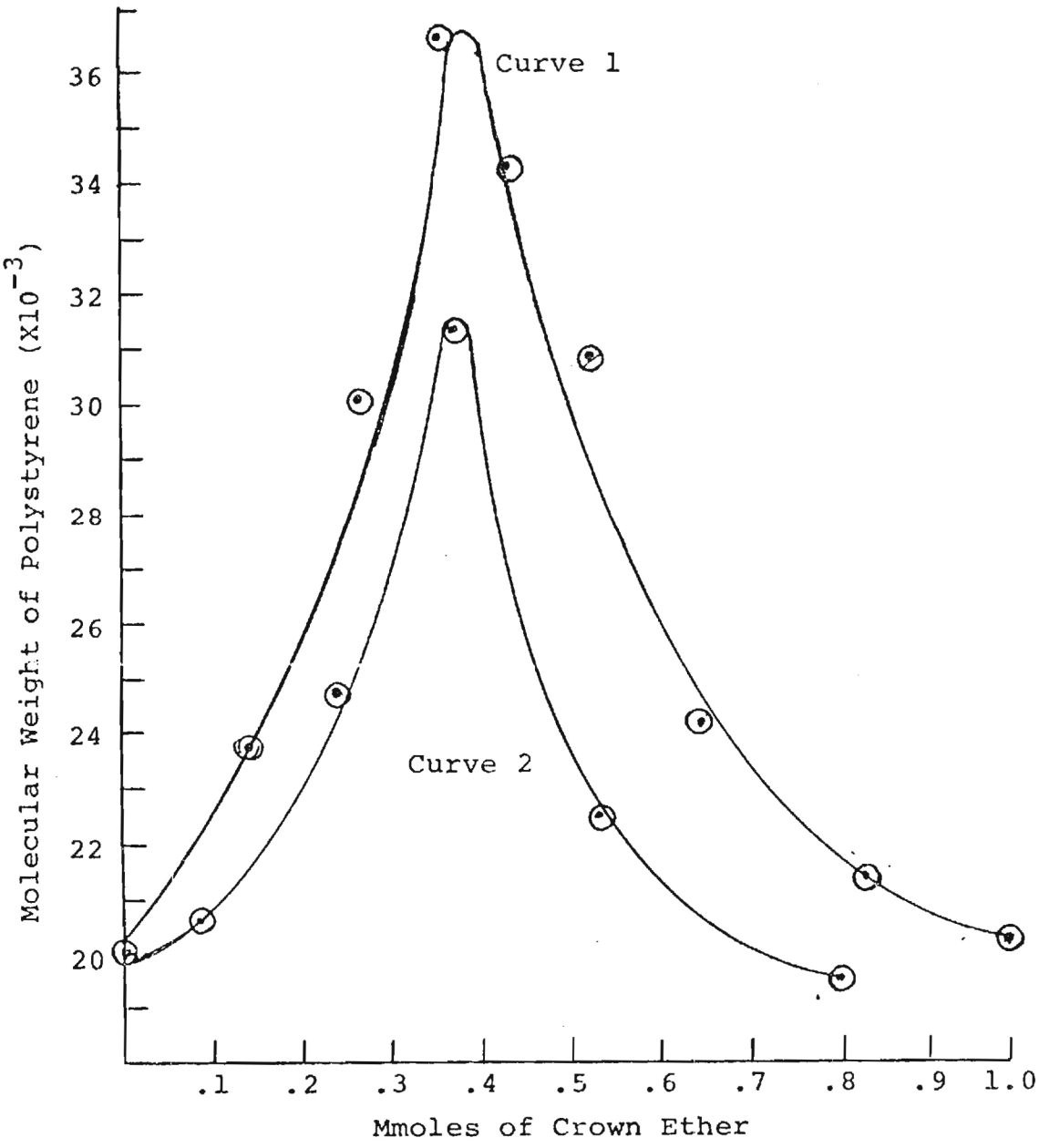

FIGURE 3. Comparison of Effects of 15-Crown-5 (Curve 1) and 12-Crown-4 (Curve 2) on Molecular Weight of Polystyrene. (Each reaction contained 0.70 Mmoles of n-BuLi.)

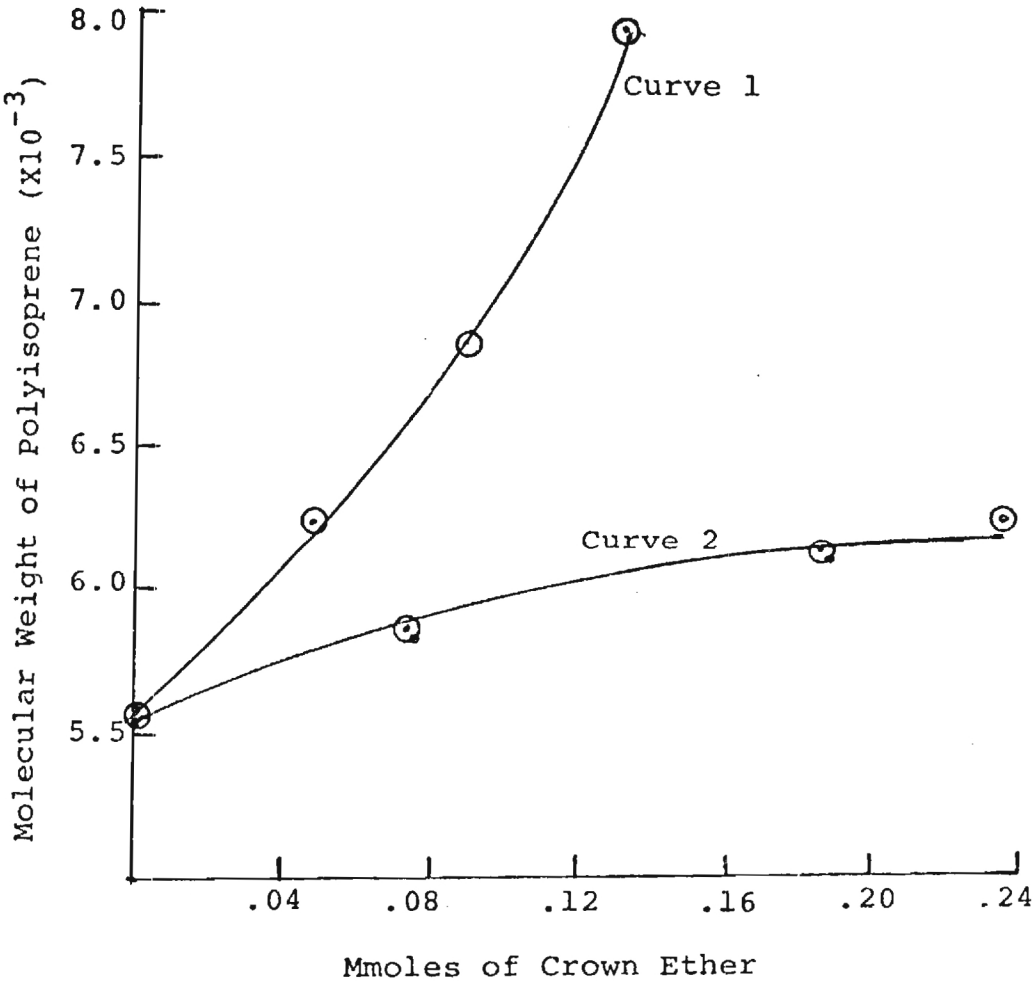

FIGURE 4. Comparison of Effects of 15-Crown-5 (Curve 1) and 12-Crown-4 (Curve 2) on Molecular Weight of Polyisoprene Using a Set 1.49 Mmoles of n-BuLi.

reach high $\overline{Mv}$ before solidification in the bulk polymerization (110^{o}-$200^{o}C$ range attempted), resulting in degradation and depletion of the catalyst. No polymer was isolated in the presence of crown ethers in the caprolactam polymerizations, whereas blank systems containing no crown ether gave good yields of polymer. A recent patent has claimed effective utilization of crown ethers in lactam polymerizations; the examples given, however, were with pyrollidone/CO_2 systems.[10]

Little effort was spent in investigating effects of crown ethers on butadiene polymerizations. The butadiene/heptane/n-BuLi/15-crown-5 and 12-crown-4 systems became viscous immediately after addition of the catalyst. However, only polymeric oils were obtained, indicating premature termination. Impurities, including oxygen and water vapor, may have been present in the butadiene and acted as chain terminators.

Further details of the research, minus the butadiene results, are contained in the copies of the thesis that accompanies this report.

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APPLICATION OF CROWN ETHERS IN INDUSTRIAL ANIONIC POLYMERIZATIONS

Final Report - Most Significant Accomplishment and Technological Impact

Dr. Fred L. Cook

The most significant research accomplishment on the project was the discovery of the extreme effects that unsubstituted crown ethers have on the polymerization characteristics of butyl lithium-initiated styrene polymerizations. Both rate of polymerization and number average molecular weight improved dramatically in the optimum crown ether systems.

Extensive rate and molecular weight studies were conducted utilizing the styrene system. When the butyl lithium catalyst was injected into the polymerization tube at room temperature, considerable heat was evolved, requiring external cooling in some cases. An orange-red tint developed in systems without crown ether when catalyst was introduced; systems containing 15-crown-5 became yellow as the quantity of crown ether was increased. The colors indicated carbanion formation, while the color change with crown ether concentration probably was due to alteration of electron density around the carbanion by virtue of the counterion complexation.

After determining that the rate of polymerization was extremely rapid in the styrene/benzene/n-BuLi/15-crown-5 system, five tubes were charged and then terminated with methanol injection as follows:

Tube	Benzene (ml)	Styrene (Mmoles)	15-Crown-5 (Mmoles)	n-BuLi (Mmoles)	Time of Reaction (sec.)	Conversion of Polymer (%)
1	15	43	0.074	0.74	10	92.5
2	15	43	0.189	0.74	10	100
3	15	43	0.063	0.74	15	100
4	15	43	0.179	0.74	30	100
5	15	43	0.00	0.74	1200	100

In the procedure used, ten seconds was the least measurable time period. The 100% conversion in Tube 2 was thus accomplished essentially instantaneously. The rate could be slowed by simply decreasing the crown ether concentration.

The rate of styrene polymerization also could be slowed by substituting 12-crown-4 for 15-crown-5. Under comparable conditions, the reaction was slowed sufficiently to obtain a rate curve with the 12-crown-4 (Figure 1). Either the 12-crown-4 was not as effective in complexing lithium cation as the 15-crown-5 (the more plausible explanation), or the strained 12-membered ring was more susceptible to cleavage at the ether linkages by the n-BuLi than was the 15-membered ring.

Both 12-crown-4 and 15-crown-5 gave a bell-shaped curve on determination of molecular weight as a function of crown concentration, with other factors held constant (Figure 2). In both cases, the molecular weight reached a maximum at a molar ratio of 0.5:1 (crown:n-BuLi). A possible explanation for the shape of the curves was based on the existence of a 1:1 complex, and relied on statistical considerations. One n-BuLi molecule initiates one growing polymer chain. When no crown ether was present in the system, all n-BuLi molecules were equivalent and initiated polymer chains which grew to a specific molecular weight in a typically narrow molecular weight distribution. When small amounts of 15-crown-5 (molar ratios of crown to n-BuLi less than 0.5:1) were added to the system, some fraction of the lithium cations were complexed while a larger portion remained uncomplexed. The growing polymer chains with complexed cations at their ends grew to longer lengths than uncomplexed charged ends due to faster kinetics and chelation stabilization, raising the average molecular weight until an optimum was reached. When molar ratios greater than 0.5:1 (crown:n-BuLi) were used, the majority of growing chains had complexed cations at their ends. The complexed chains again grew faster than those associated with uncomplexed cations, but with the rapid depletion of, and competition for, monomer being the limiting factor in their growth, the average molecular weight was not allowed to reach the previous peak values. Since the number of complexed chain ends in these systems was greater than the number in the optimum system (molar ratio of crown to n-BuLi $\leq$ 0.5:1), each polymer chain contained fewer monomer molecules due to rapid monomer depletion, and the average molecular weight dropped from its peak value. In those systems employing a molar ratio of crown to n-BuLi approaching unity, all initiator molecules were again near equivalence (nearly all

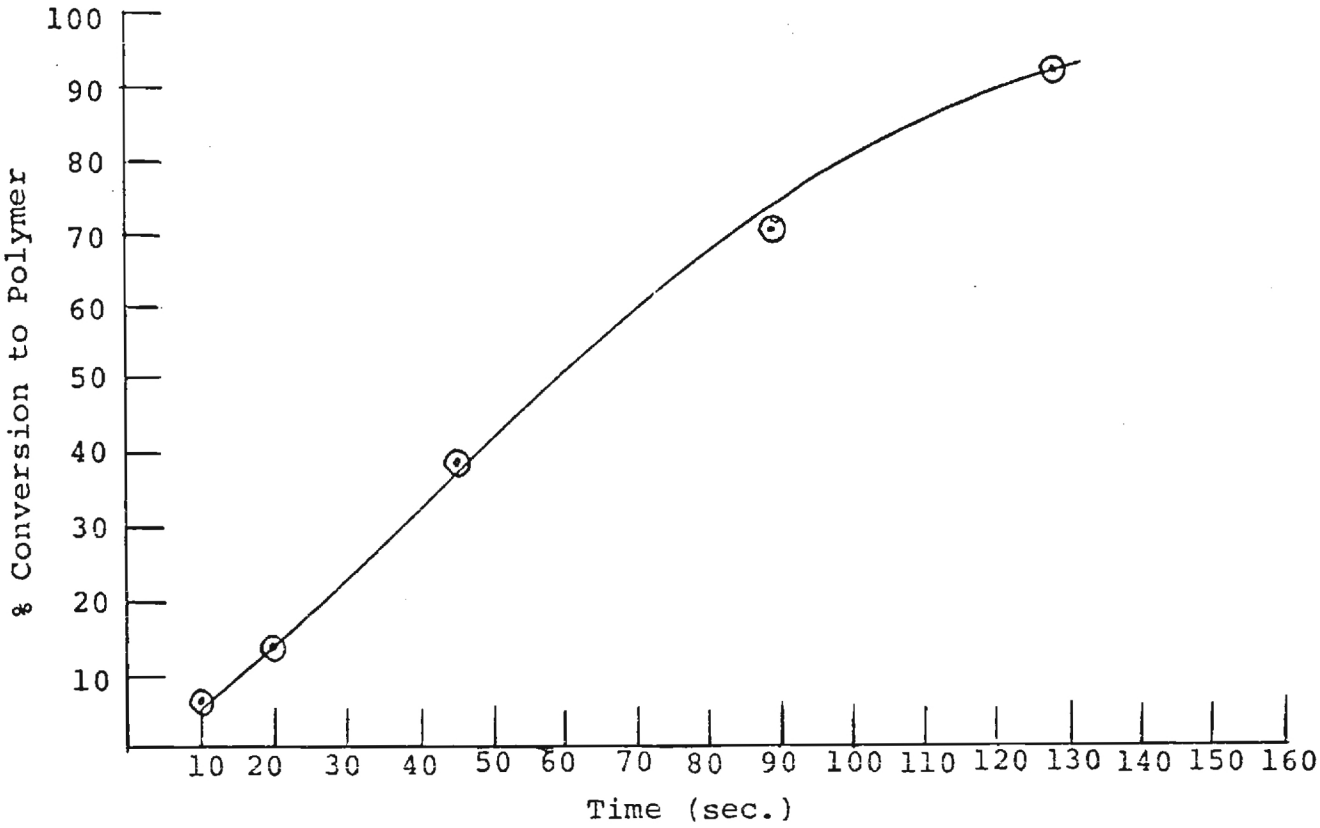

FIGURE 1. Overall Rate Study for Polymerization of Styrene Using 12-Crown-4. Each Reaction contained 0.035g of 12-Crown-4 (.01M).

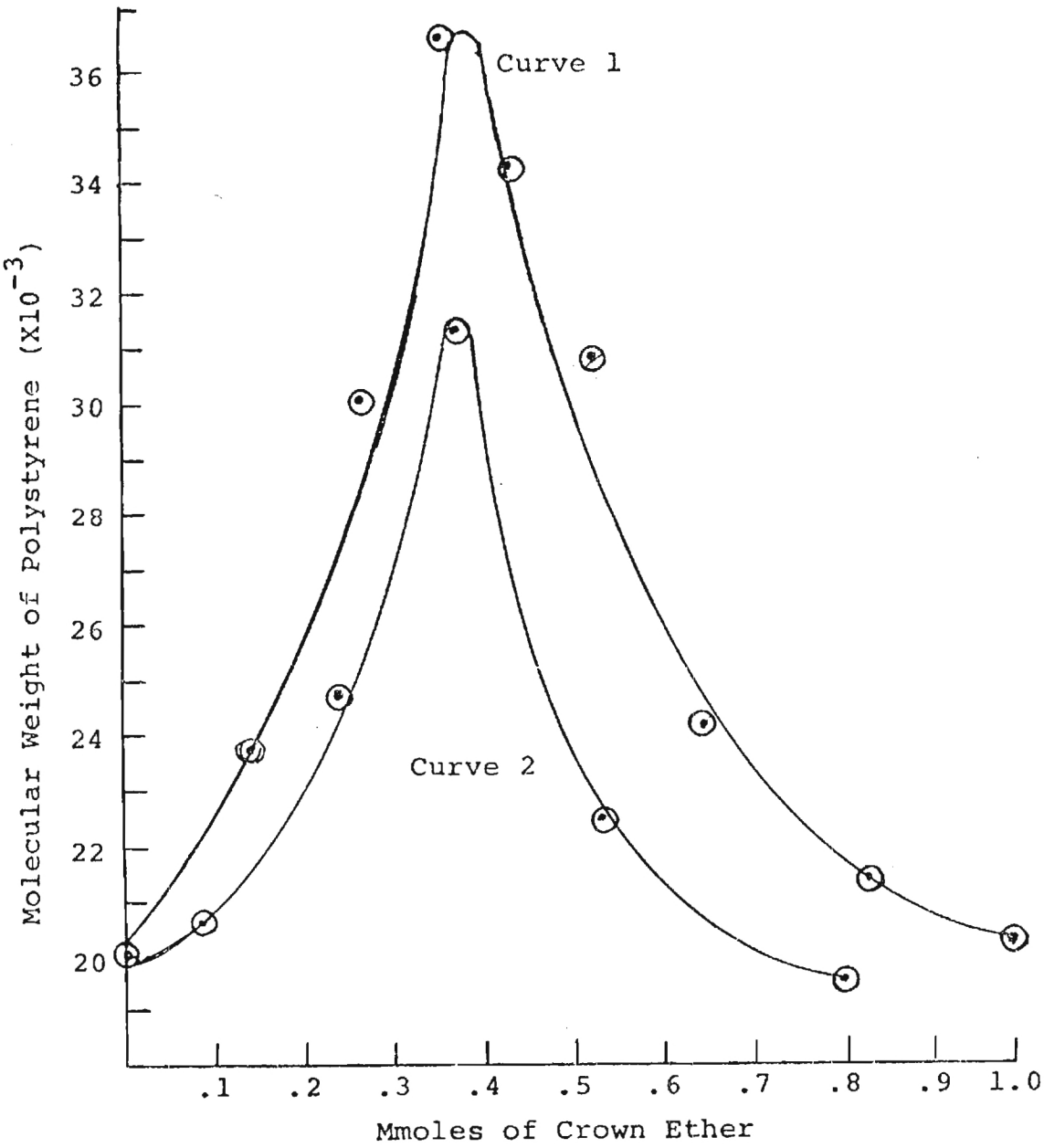

FIGURE 2. Comparison of Effects of 15-Crown-5 (Curve 1) and 12-Crown-4 (Curve 2) on Molecular Weight of Polystyrene. (Each reaction contained 0.70 Mmoles of n-BuLi.)

complexed) and the chains grew to the molecular weight obtained when none were complexed. In the completely uncomplexed systems, limitation of molecular weight was thus due to chain end instability due to disproportionation and susceptibility to termination by impurities. In systems in which all the counterions were complexed, the 1:1 complex theory dictates that the depletion of monomer prevented the complexed chains from growing to the long lengths required for high molecular weight.

The molecular weight of polystyrene also depends on the concentration of n-BuLi. Figure 3 details the variation of inherent viscosity as a function of n-BuLi concentration. Curve 1 polymerizations contained no crown ether, while the Curve 2 polymerizations contained a fixed concentration of 15-crown-5. The shapes of the two curves are basically the same; however, the crown ether had the effect of shifting the curve upward on the inherent viscosity scale.

The research results indicate that in-mold bulk polymerization of styrene with the crown-butyl lithium catalyst system may be feasible. The extremely rapid rate of polymerization and ability to "tailor" the molecular weight by the crown concentration offers molding capabilities. In addition, the increase in rate of isoprene polymerization with crown ethers offers the potential of modifying the styrene with diene comonomer during in-molding processing and thus improving its impact resistance. Application of crown ethers in recently-developed solution polymerizations with n-BuLi, such as SBR block rubbers (e.g., Phillips Petroleum's K-Resins KR-01 and KR-03) and SBS tri-block rubbers (e.g., Phillips Petroleum's Solprene 308), may be feasible to improve productivity and molecular weight. Another potential commercial application is in copolymerization of styrene with unsaturated polyester resins, a common system used in molding of fiberglass-reinforced composites. In-mold bulk polymerization with styrene, styrene/butadiene solution polymerization, and application to fiberglass composites offer significant opportunities for crown ethers to make a meaningful technological impact on engineering practice and industry based on the reported research.

Further details of the styrene research are contained in the copies of the thesis accompanying this report.

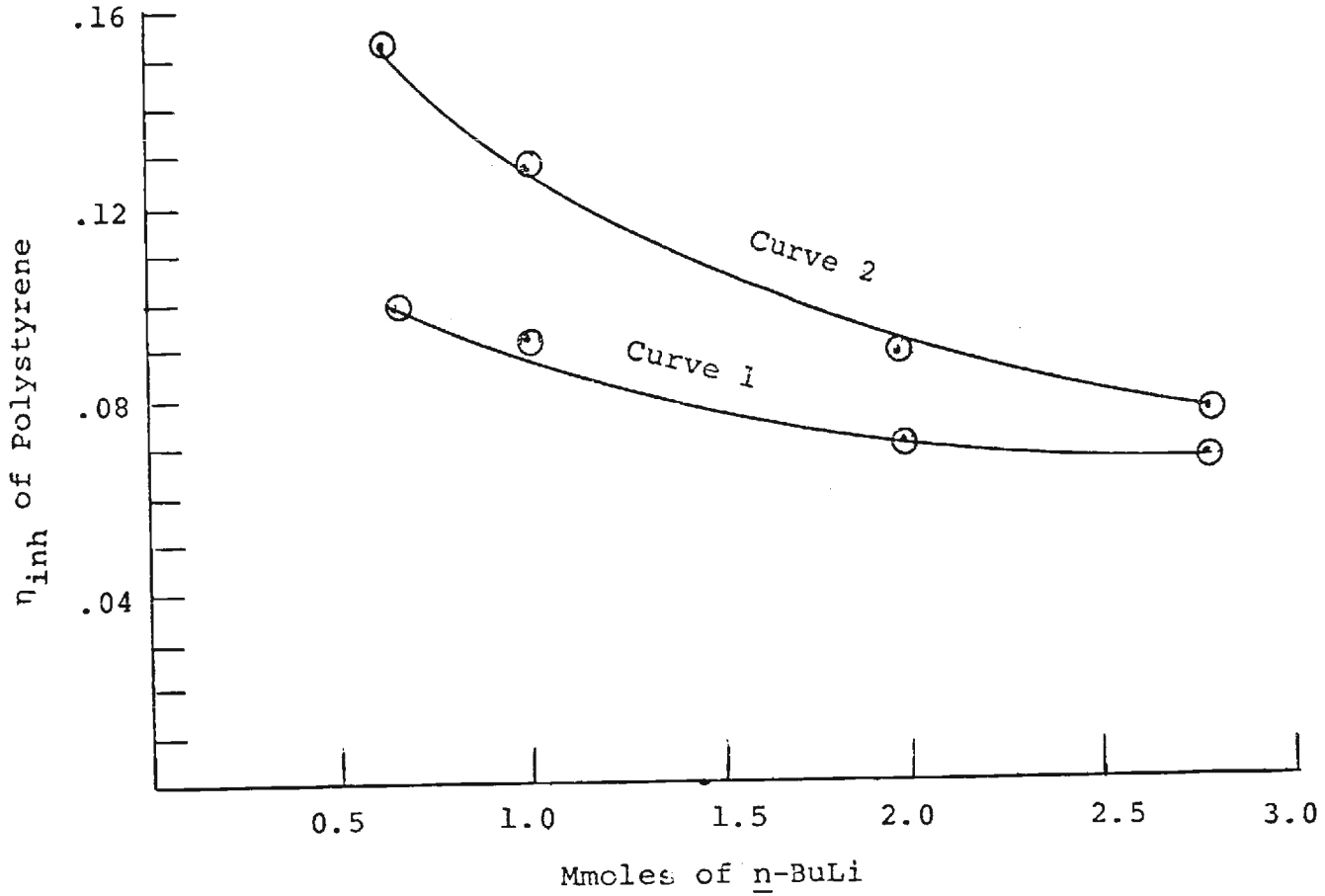

FIGURE 3. Effect of Concentration of n-BuLi on η_{inh} of Polystyrene. Reactions in Curve 1 Contained No Crown. Reactions in Curve 2 Contained 0.19 Mmoles of 15-Crown-5.

APPLICATION OF CROWN ETHERS IN INDUSTRIAL
ANIONIC POLYMERIZATIONS

Final Report - Auxiliary Personnel

Dr. Fred L. Cook

In addition to the Principal Investigator, three students have participated in the project. Mr. Kenneth Domeshek, an undergraduate, was supported through the project in the summer of 1976. He participated in the studies aimed at improving yields and isolating and purifying the crown ethers utilized in the polymerization research. He also aided in initial attempts to synthesize unsubstituted 14-crown-4 and purified many of the solvents and reagents needed in the polymerization studies. Mr. Domeshek made substantial contributions to the project while expanding his own research capabilities and expertise.

Mr. Thomas Montgomery and Mr. Robert Burton participated on the project for their M.S. thesis research. The two students were supported through the School of Textile Engineering, and not through the project. Mr. Montgomery was invaluable in the initial polymerization studies, offering numerous suggestions to alter the approaches and proving to be an excellent experimentalist. He gained valuable experience in polymerization techniques and polymer analysis, thus enabling him to broaden his career opportunities and capabilities as a chemist. He is currently employed as a polymer research chemist with American Enka Corporation. The thesis submitted for graduation by Mr. Montgomery is included with this report. Mr. Burton is scheduled to graduate in December of 1978, and has concentrated on completing the work begun by Mr. Montgomery and expanded the research into the butadiene area. As part of his thesis research not connected with the reported project, he is investigating other crown ether-complexed metal salts (sodium acetate, sodium cyanide, etc.) as alternatives to n-BuLi in anionic polymerizations, and is comparing a lithium-complexing aza crown ether, 18-aza-crown-6, to the oxa crown ethers utilized in the reported investigation.

APPLICATION OF CROWN ETHERS IN INDUSTRIAL
ANIONIC POLYMERIZATIONS

Final Report - Papers, Presentations, Awards

Dr. Fred L. Cook

Dr. Fred L. Cook, Principal Investigator on the project, has expanded his professional activities considerably during the 1976-1978 reporting period. Dr. Cook has obtained nine sponsored projects during the period:

1. "Energy Conservation in the Textile Industry", Department of Energy, $356,446, June 1976-August 1978, (Co-Principal Investigator--responsible for the Textile Engineering effort on the project, which included three additional professors, two technicians, and several part-time technicians and graduate students).
2. "Application of Crown Ethers in Industrial Anionic Polymerizations", National Science Foundation, Faculty Research Initiation Program, $20,000, June 1976-March 1978 (Sole Investigator--responsible for entire scope of project; supervised one full-time technician for part of the project, and two graduate students).
3. "Preparation and Analyses of Chemically Sorptive Yarns from Rayon and Acrylic Precursors", U. S. Army-Natick Laboratories, $19,736, September 1976-March 1978, (Principal Investigator--responsible for the technical and management aspects of the project; included one additional professor, one full-time technician, and one graduate student).
4. "State Industrial Energy Extension Program: Textile Sector", Office of Energy Resources, August 1977-December 1978, (Investigator--responsible for the wet processing sector of the project; divided textile plant responsibilities with the principal investigator).
5. "Selected Modifications of Nylon 6", Allied Chemical Company, $25,000, March 1978-December 1978 (Sole Investigator--responsible for entire scope of project; supervised one post-doctoral fellow, one graduate student, and two special problems students.
6. "In-Plant Demonstration of Dyebath Reuse Applied to Hosiery Dyeing", Department of Energy, $74,856, June 1978-December 1978, (Senior Investigator--overall responsibility for formulating and executing the technical research plan; includes two additional professors, one technician, two engineers and plant personnel).
7. "Equipment for Specialized Polymer Research", National Science Foundation, $11,317, July 1978 (Sole Investigator--responsible for purchase, maintenance, and utilization of the equipment).

8. "Machnozzle/Can Drying", Department of Energy, $101,000 August 1978-August 1979 (Consultant--responsible for effect of new drying techniques on the quality of dyed and finished textiles).

9. "Application of Dyebath Reuse to Jet Dyeing of Fabric", Georgia Tech Administration, $21,663, August 1978-August 1979 (Principal Investigator--responsible for the technical and management aspects of the project; includes one additional professor and one technician).

He has made numerous invited presentations including:

1. "Energy Conservation in the Textile Industry", American Textile Manufacturer's Institute Meeting, Charlotte, N. C., 1976.

2. "Energy Consumption by Wet Process", National Meeting, Textile Information Users Council, Atlanta, Georgia, 1976.

3. "Dyebath Reuse in Carpet Beck Dyeing", National Meeting, American Chemical Society, New Orleans, Louisiana, 1977.

4. "Studies of Crown Ether Complexes. II. Crystalline Complexes of 18-Crown-6 with Various Nitrile Compounds", First Symposium on Macrocyclic Compounds, Brigham-Young University, Provo, Utah, 1977.

5. "Energy Consumption and Energy Conservation Potential of Textile Wet Processes", ASME Meeting, Greenville, S. C., 1977.

6. "Utilization of Dyebath Reuse in Batch Dyeing", AATCC International Technical Conference, Atlanta, Georgia, 1977.

7. "How to Conserve Energy in Wet Processing", EES Energy Conservation Systems Workshop for Plant Engineers, Dalton, Georgia, 1976.

8. "Dyebath Reuse Applied to Hosiery, Pressure Package, and Fabric Dyeing", Clemson Wastewater Conference, Hilton Head, S. C., 1978.

9. "Degradation of PAN Models and Crown Ether Chemistry", Monsanto Fibers Research Center, Durham, N. C., 1977.

10. "Dyebath Reuse Applied to Carpet Processing", CRI Annual Technical Conference, Destin, Florida, 1977.

11. "Dyebath Reuse in Batch Dyeing", National Meeting, American Chemical Society, to be held in Miami, Florida, 1978.

12. "Application of Crown Ethers in Industrial Anionic Polymerizations", Second Symposium on Macrocyclic Compounds, to be held at Brigham-Young University, Provo, Utah, 1978.

13. "Synthesis and Applications of Crown Ethers", Atlanta University, Morehouse College, 1976.

14. "Energy Consumption in the Textile Industry", Georgia Tech, 1976.

15. "Energy Consumption by Wet Process", Annual Meeting, Textile Operating Executive, Atlanta, Georgia, 1976.

16. "Preparation and Synthetic Utilization of Crown Ethers", Chemistry Department, Berry College, Rome, Georgia, 1977.

17. "Fundamentals of Dyeing", Short Course, American Association of Textile Chemists and Colorists, Southeast Regional Conference, Atlanta, Georgia, 1976.

18. "Fundamentals of the Dyeing Process", Short Course, American Association of Textile Chemists and Colorists, South Central Section Meeting, Dalton, Georgia, 1976.

19. "Energy Consumption by Process in Dyeing and Finishing", Short Course, Clemson University, Clemson, S. C., 1976.

20. "Finishing Fundamentals", Short Course, School of Textile Engineering, Auburn University, Auburn, Alabama, 1977 and 1978.

21. "Application of Crown Ethers in Industrial Anionic Polymerizations", School of Chemistry, Mercer University, Macon, Georgia, 1978.

22. "Fundamentals of the Dyeing Process", Chemistry Department, Berry College, Rome, Georgia, 1978.

23. "Energy Consumption in Wet Processing and Routes to Conservation", College of Textiles, N. C. State University, Raleigh, N. C., 1978.

24. "Crown Ether Chemistry", Chemistry Department, Oglethorpe College, Atlanta, Georgia, 1976.

Dr. Cook has had the following papers accepted for publication in the 1976-1978 reporting period:

1. Cook, F. L.,* and Tincher, W. C., "Dyebath Reuse in Batch Dyeing", Textile Chemist and Colorist, 10(1), 21/1, 1978.

2. Cook, F. L., Harris, H. P., Gokel, G., Liotta,* C. L., and Cram, D. J.,* "Macrocyclic Polyether: 18-Crown-6 Polyether", chapter in "Organic Syntheses", Vol. 57, p. 30, 1978.

3. Cook, F. L., Perkins, W. S.,* et al., "The Effect of Variations in Bleaching on the Dyeability of Cotton Fabrics", Textile Chemist and Colorist, 9(12), 16/281, 1977.

4. Cook, F. L.,* and Tincher, W. C., "Dyebath Reuse in Carpet Beck Dyeing", ACS Abstracts of Papers, 1973 (1977).

5. Cook, F. L.,* and Tincher, W. C., "Dyebath Reuse in Batch Dyeing", AATCC Book of Papers, 145 (1977).

6. Cook, F. L., Perkins, W. S.,* et al., "A Study of the Effect of Peroxide Concentration of Alkalinity Variations in Bleaching on the Dyeability of Cotton Fabrics with Direct Dyes", AATCC Book of Papers, 25 (1977).

*Denotes principal author.

7. Cook, F. L.,* and Tincher W. C., "Dyebath Reuse in Carpet Beck Dyeing", Cellulose, Paper and Textile Chemistry Preprints, American Chemical Society, 1973, 1 (1977).

8. Cook, F. L.,* and Tincher, W. C., "Dyebath Reuse in Batch Dyeing", ACS Abstracts of Papers, 1978 (in press).

9. Cook, F. L.,* and Dawkins, J., "Energy Conservation in the Textile Industry, Phase I Report", Department of Energy, April, 1977, "Quarterly Reports", 1976-present; Phase II Report, August, 1978.

10. Cook, F. L.,* "Preparation and Analysis of Chemically-Sorptive Yarns", USA-Natick Laboratories, Monthly Reports, 1976-present; "Final Report", July, 1978.

11. Cook, F. L.,* "Application of Crown Ethers in Industrial Anionic Polymerizations: Annual Report", National Science Foundation, 1977; "Final Report", July 1978.

12. Cook, F. L., Lowry, J. L.,* et al., "A Study of Barriers to Commercialization of Energy Conservation Technology in the Textile Industry", Final Report with Argonne National Laboratories, Department of Energy, 1977.

Dr. Cook has been elected as a Full Member to Sigma Xi, the Scientific Research Society of North America. He is also a member of the Delta Kappa Phi Textile Honorary Fraternity, Tau Beta Pi Engineering Honorary Fraternity, American Chemical Society, and the American Association of Textile Chemists and Colorists.

*Denotes principal author.

NATIONAL SCIENCE FOUNDATION
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SUMMARY OF COMPLETED PROJECT

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1. INSTITUTION AND ADDRESS	2. NSF PROGRAM	3. PRINCIPAL INVESTIGATOR(S)
GEORGIA INSTITUTE OF TECHNOLOGY School of Textile Engineering Atlanta, Georgia 30332	Engineering Research Initiation Grant	Dr. Fred L. Cook

4. AWARD NUMBER	5. DURATION (MOS)	6. AWARD PERIOD	7. AWARDEE ACCOUNT NUMBER
ENG76-10141	18	from 4/76 to 3/78	

8. PROJECT TITLE

Application of Crown Ethers in Industrial Anionic Polymerizations

9. SUMMARY (ATTACH LIST OF PUBLICATIONS TO FORM)

The effects of the addition of catalytic quantities of macrocyclic polyethers (crown ethers) to anionic-initiated polymerization systems were investigated. Dramatic modifications in the polymerization characteristics of the n-BuLi-styrene-benzene system occurred upon the addition of 15-crown-5. Complete conversion to polymer was obtained in systems containing the complexing agent in less than ten seconds (the least possible measurable time under the employed experimental procedure). The molecular weight of polystyrene produced from the modified system increased to an optimum value as the molar ratio of crown ether to n-BuLi approached 0.5:1. Further addition of the crown ether (molar ratio greater than 0.5:1) caused a decrease in the molecular weight to the same low values obtained in systems containing no complexing agent. The addition of 12-crown-4 to the system produced effects of a lesser magnitude in both the overall rate of polymerization and the molecular weight of the polymer, but the benefits over systems containing no crown were substantial.

The results of the research indicate that in-mold polymerization of styrene with the crown/n-BuLi catalyst system may be feasible. The extremely rapid rate of polymerization and the ability to "tailor" the molecular weight by varying the crown concentration offer potential in-mold polymerization capabilities that have not been previously defined in the literature.

Moderate increases in the molecular weight of polyisoprene were obtained by the addition of either 15-crown-5 or 12-crown-4 to the n-BuLi-isoprene-heptane polymerization system. Through use of 12-crown-4, the reaction time to reach 100% conversion to polymer was reduced by 67%, while the addition of 15-crown-5 to the system allowed the time of reaction to be reduced by 83% in comparison to systems containing no crown ether.

Attempts to modify polymerization systems employing n-BuNa as an initiator through use of crown ethers proved unsuccessful. Likewise, attempts to modify the bulk anionic polymerization of caprolactam by addition of crown ethers proved unsuccessful due to instability of the crown ethers under the polymerization conditions. Polymerizations with butadiene produced low-molecular weight material, apparently due to gaseous impurity problems in the monomer that were not resolved in the reported research.

9. SIGNATURE OF PRINCIPAL INVESTIGATOR/ PROJECT DIRECTOR	TYPED OR PRINTED NAME	DATE
	Dr. Fred L. Cook	7/25/78

NSF Form 98A (10-77) SUPERSEDES ALL PREVIOUS EDITIONS